REMARKS

Claims 1, 4-5, and 7-15 are pending in the application. Claims 1 and 7 have been amended, and claims 2-3 and 6 have been cancelled. Further, claims 8-15 are newly added to the application in order that the Applicants may more fully claim the subject matter of their invention.

The specification has been amended to place the specification in standard form. Additionally, several minor typographical errors have been corrected. In view of the changes to the original specification, a substitute specification and abstract including the changes and rendered in paragraph numbered format is attached hereto. Entry of the substitute specification and abstract is respectfully requested. No new matter has been introduced by the amendment.

Claim Objection

An objection has been raised to claim 6 in view of the recitation of an Mn concentration beyond that recited in independent claim 2. This objection is now moot in view of the cancellation of claims 2 and 6.

Rejection Under 35 U.S.C. § 102(b)

Claim 1 has been rejected over Japanese Patent Publication 5-190183 ("the '183 publication"). This rejection is believed overcome in view of the amendment of claim 1 together with the following remarks.

Claim 1, as amended, recites and electrochemical cell that includes an electrode in which a portion of the electrode extending less than 20 microns from the electrolyte comprises 0.5 to 6 metal atom % Mn. Claim 1 further recites that the remaining portions of electrode comprise substantially less than 6 metal atom % Mn. The applicants respectfully assert that the '183 publication does not suggest or disclose an electrochemical cell as recited by claim 1. Although the '183 publication discloses an electrode containing Mn in a molar ratio of 5-50 mol%, there is no suggestion within the '183 reference that the concentration of Mn be limited within a range of 0.5 to 6 metal atom % within a specified distance from the electrolyte. Further, there is no suggestion

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within the '183 publication that portions of the electrode beyond a specified distance from the electrolyte include substantially less than 6 metal atom % Mn.

The applicants respectfully assert that the Mn concentration characteristics recited in claim 1 and in the applicants' remaining pending claims provide an electrochemical cell having improved integrity and operating performance. Further, the applicants respectfully assert that the benefits arising from the applicants' claimed electrochemical cell encompass unexpected results for YSZ electrochemical cells. As set forth in the accompanying declaration of Dr. Mogensen, an electrode having relatively small concentration of Mn in a portion of the electrode extending less than about 20 microns from the electrolyte produces a solid-oxide-fuel-cell ("SOFC") having improved performance characteristics. (Mogensen Declaration, para. 3). The construction of a nickel-based electrode having a limited Mn concentration provides a electrochemical cell having less polarization resistance. The improvement is most noticeable in the electrochemically active portion of the electrode. *Id.* Further, the in-plane conductivity of Ni-based electrodes having a relatively small concentration of Mn is also improved. (Mogensen Declaration, para. 4).

In experimentation with thin-electrolyte SOFC devices, unregulated addition of Mn resulted in poor mechanical stability including electrode delamination. (Mogensen Declaration, para. 6). In attachment A to Dr. Mogensen's declaration, experimental results are set forth showing a substantial degree of Nn migration to the anode-electrolyte interface. As set forth in attachment A, the authors attribute the observed delamination to a weakening of the interface.

The applicants' respectfully assert that none of the above characteristics are suggested or disclosed by the '183 publication. Accordingly, the applicants respectfully assert that claim 1 fully distinguishes over the '183 publication and is in condition for allowance.

Rejection Under 35 U.S.C. § 103(a)

Claims 4 and 5 have been rejected over the '183 publication. This rejection is believed overcome in view of the amendment of claim 1 together with the following remarks.

The applicants' foregoing remarks pertaining to the '183 publication are incorporated by reference herein. Claims 4 and 5 depend directly and indirectly, respectively, from claim 1. Accordingly, these claims are believed allowable in view of their dependence from claim 1.

In response to the remarks set forth at page 4 of the instant Office Action, the applicants assert that Figure 4 in the '183 publication does not anticipate or render obvious their claimed invention. The applicants respectfully assert that no amount of analysis applied to Figure 4 of the '183 publication would suggest to one skilled in the art that the Mn concentration profile within the electrode relative to a particular distance from the electrolyte. Figure 4 of the '183 publication merely shows an improvement in polarization resistance as the concentration of Mn increases. The applicants respectfully assert that the disclosure of reducing polarization resistance as a function of an increase in Mn concentration fails to inform one skilled in the art of the particular benefit obtained by the claimed Mn concentration profile relative to the electrolyte.

Claims 1-2 and 6-7 have been rejected over Ruka et al. in view of JP 5-190183. This rejection is believed overcome in view of the amendment of claim 1 together with the following remarks.

The Applicants' foregoing remarks pertaining to the '183 publication are incorporated by reference herein. The Applicants respectfully assert that the addition of Ruka et al. does not overcome the deficiency of the '183 publication. Neither Ruka et al. nor the '183 publication suggest or disclose an electrochemical cell in which the electrode has an Mn concentration within the recited concentration range in a portion of the electrode extending less than 20 microns from the electrolyte. Applicants respectfully assert that the disclosure by Ruka et al. of an electrode having a total thickness of less than about 180 micron, and more preferably about 100-150 microns, does not suggest or disclose an electrode having 0.5 to 6 metal atom % Mn extending less than 20 microns from the electrolyte. This is at least because that there is no disclosure within either Ruka et al. or the '183 publication of a need to limit the Mn concentration to avoid mechanical stability problems (see Moegensen Declaration, para. 6).

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The rejection of claims 2 and 6 is now moot in view of the cancellation of those claims.

Claim 7 is believed allowable in view of the amendment and remarks pertaining to claim 1 from which it depends.

New Claims

Claims 8-15 are newly added in order that the applicants may more fully claim the subject matter of their invention. Claim 8 recites an electrochemical cell having a first layer overlying the electrolyte and at least one additional layer. The first layer comprises 0.5 to 6 metal atom % Mn, and the at least one additional layer comprises substantially less than 6 metal atom % Mn. The applicants respectfully assert that the electrochemical cell recited in claim 8 is not suggested or disclosed by the cited references, taken alone or in combination.

Claim 9 depends from claim 8 and recites that the first layer comprises 1-4 metal atom % Mn. This claim is believed allowable in view of its dependency from claim 8.

Claim 10 depends from claim 8 and recites that the first layer comprises 2-3 metal atom % Mn. This claim is believed allowable in view of its dependency from claim 8.

Claim 11 recites a solid oxide fuel cell in which the electrode comprises an active layer having a thickness of no more than 20 microns and comprising 0.5 to 6 metal atom % Mn. This claim is believed allowable in view of the failure of the cited references to suggest or disclose an electrode having an active layer of a specified thickness and a particular Mn concentration range within the active layer.

Claim 12 depends from claim 11 and recites that the active layer comprises 1-4 metal atom % Mn. This claim is believed allowable in view of its dependence from claim 11.

Claim 13 depends from claim 11 and recites that the active layer comprises 2-3 metal atom % Mn. This claim is believed allowable in view of its dependence from claim 11.
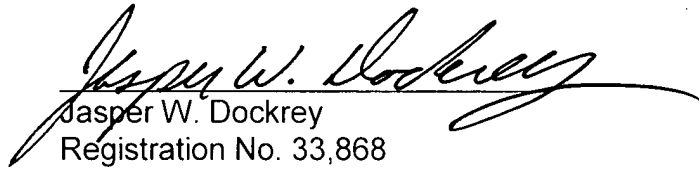
Claim 14 depends from claim 11 and recites that the solid oxide fuel cell comprise additional electrode layers overlying the active layer. This claim is believed

allowable in view of its dependence from claim 11 and further in view of the failure of the prior art to suggest or disclose additional electrode layers overlying an active layer.

Claim 15 depends from claim 14 and recites that the additional layer comprise electrode materials having substantially less than 6 metal atom % Mn. This claim is believed allowable in view of its dependence from claim 14 and further in view of the failure of the prior art to suggest or disclose additional layers overlying the active layer that have an Mn concentration within the specified range.

The Applicants have made a novel and nonobvious contribution to the art of electrochemical cell fabrication. The claims at issue distinguish over the cited references and are in condition for allowance. Accordingly, such allowance is now earnestly requested.

Respectfully submitted,

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ELECTROCHEMICAL CELL

TECHNICAL FIELD

[0001] The invention relates to an electrochemical cell, such as an SOFC cell, comprising a nickel based electrode structure, such as in form of an Ni/YSZ anode, to which Mn has been added.

BACKGROUND ART

[0002] It is known from JP 5-190183 to add Mn to the Ni/YSZ anode in an amount of 5 to 50 metal atom % of the anode material. As a result the reaction resistance (R_P) of the anode is reduced.

[0003] The composite Ni/YSZ electrode for SOFC has been the object of several optimizing studies with respect to microstructure, particle size relationship, sintering temperature and quantitative ratio of the two materials. Ni/YSZ composite anodes are known with a reaction resistance R_P lower than 0.10 to 0.15 Ωcm^2 at 1000°C in hydrogen with approximately 3% water.

[0004] An R_P lower than above has been obtained by using ruthenium in stead of nickel, but ruthenium is relatively cost intensive and difficult to process for the purpose.

[0005] In stead of the typical ZrO_2 based electrolyte, it is possible to use a mixed conductor based on for instance PrO_x and CeO_2, whereby the R_P is reduced. Again, the raw materials are relatively expensive.

[0006] The demand for a high conductivity in the electrode can be met by using an Ni/YSZ composite with a high content of Ni or by sintering the electrode structure at a high temperature in such a manner that the nickel particles are brought into a good contact. However, it is not advantageous to have a too high content of nickel because the thermal coefficient of expansion (TEC) of the electrode is thereby increased. As a result it moves away from the electrolyte both in the oxidized state and in the reduced state. Furthermore, it has been demonstrated that fractures caused by the difference in TEC easily propagate between the electrode and the compactly sintered electrolyte when the sintering

temperature is higher than stated above. Finally, the content of Ni should be low in order to minimize the tension in the structure in case the nickel content of the electrode unintendedly oxidizes during operation.

[0007] No technically suitable method is known for lowering the catalytic properties of nickel apart from a lowering of the nickel content/the nickel surface, which in general has a negative effect on the polarization resistance R_P of the electrode and the electric conductivity.

DEFINITION OF PROBLEMS

[0008] A) An improvement of the efficiency of the electrochemical cell and a reduction of the costs give rise to a demand for reducing the power loss ($W_{TAB}=R_P i^2$) associated with the electrode process and below expressed by the reaction resistance R_P also called the polarization resistance. It turned out that an Ni/YSZ composite electrode with respect to function, but not necessarily to production can be divided into two zones with different primary functions. The electrode is electrochemically active in a range of 10 to 20 μm from the compactly sintered electrolyte, which means that here the reactants are reacted by way of oxidation reduction while releasing or receiving electrons. This layer is associated with the lowest achievable reaction resistance RP for the electrode in question.

[0009] B) The primary function of the superposed electrode structure is contacting and as electron conductor because the reactants in the active layer are only reacted in so far as electrons can be transmitted to or from the electrode. This conductivity is substantial because a predetermined distance of the magnitude of mm or more can exist in the technical structure of the electrochemical cell between the contact points of the electrode and the structure establishing the electric contact to the cell.

[0010] C) As far as an SOFC driven on natural gas or methane is concerned, the endothermal steam reforming reaction should for optimizing reasons be carried out on or adjacent to the active cell where heat is generated. The strong catalytic properties of nickel have the effect that the steam reforming reaction on a nickel based electrochemical cell typically occurs over the first few mm of the electrode

adjacent the gas inlet, whereby this part of the system is strongly cooled. As a result, thermal gradients arise in the system which in turn involves a risk of breaking. Accordingly there is a demand for a possibility of suppressing the activity of a specific amount of nickel in the electrode with respect to the catalytic reaction of hydrocarbons. This demand applies to the entire electrode structure and primarily to the superposed electrode part which handles the conductivity of the electrode as this part presents the largest nickel surface.

BRIEF SUMMARY

[0011]   The above three problems can to a considerable degree be solved by adding MnO_x to the nickel based electrode or the nickel based catalytic component. Here and below the expression MnO_x is used for all possible components which can supply the element Mn bearing in mind that under usual operational conditions for such structures nothing but Mn-oxides or a mixed metallic oxide containing Mn exist.

[0012]   The object of the present invention is to show how the reaction resistance R_P can be further reduced as well as how further advantages in form of an increased conductivity and a limited catalytic activity can be obtained.

[0013]   An electrochemical cell of the above type is according to the invention characterized in that the added amount of Mn represents 0.5 to 5 metal atom%, preferably 1 to 4 metal atom%, especially 2 to 3 metal atom%.

[0014]   An electrochemical cell can be produced by applying electrodes onto a carrier electrolyte or electrolyte on a carrier electrode. The cell can be produced by intermediate sinterings or be sintered when more or all the components are assembled.

[0015]   An electrochemical cell can be used within several fields, said cell comprising an electrolyte, which is also called a membrane, in contact with two electrodes of a predetermined composition where at least one electrode is subjected to a gas mixture which has a reducing effect compared to air. Below four examples are presented of how the electrochemical, electric and catalytic

properties of such a nickel based electrode are of vital importance for the efficiency of the cell.

[0016] i) a solid oxide fuel cell (SOFC) is a catalytic cell mainly comprising an electrolyte with an anode and a cathode on opposed sides. A nickel electrolyte composite is widely used as the anode. The electrolyte is most frequently a Y-doped ZrO_2 (YSZ). The anode is most frequently produced by way of sintering in air, the reason why NiO is used. During operation the NiO is reduced to Ni in the reducing anode gas. The fuel cell can be supplied with a gas, such as hydrogen or methane, and produce current or be driven by means of the current and dissociate for instance water or carbon dioxide.

[0017] ii) An electrochemical reactor can be used for a chemical synthesis by way of a complete or partial oxidation of a compound, such as for instance methane, ethane or methanol. The reactor can be based on electrochemical cells with two electrodes, where at least one electrode, viz. the active electrode, catalyzes the oxidation. This electrode is typically nickel based.

[0018] iii) An oxygen separation membrane can be used for the production of for instance synthesis gas by way of a partial oxidation of for instance methane. This membrane can be a dense electrolyte as stated above or an electrolyte which has been provided with an electronic conductivity, viz. be internally short circuited, and on which a nickel based electrolyte catalyzes the oxidation. A reactant, such as for instance oxygen, water or carbon dioxide can be mixed into the reducing gas or oxygen can be supplied in ionic form through the membrane. This process can be electrically driven by transmitting a current through the cell, viz. the compact electrolyte, or the cell can be internally short circuited, viz. the electrolyte with the electronic conductivity.

[0019] iv) As a sensor for measuring the composition of the gas.

[0020] In the four examples i)to iv) the nickel based electrode has been subjected to a reducing atmosphere, in which a complete or partial oxidation or reduction of a reactant takes place. The fundamental function of the electrochemical cell is thus to oxidize for instance methane, hydrogen or carbon monoxide while delivering an electric current, or to drive the process in the

opposite direction by applying a current and dissociating for instance water into hydrogen and oxygen.

[0021] The efficiency of the electrode is typically defined by the following three values: A) the power loss associated with the electrode process, B) the electric conductivity of the electrode, and C) the catalytic activity of the electrode.

BRIEF DESCRIPTION OF THE DRAWINGS

[0022] The invention is explained in greater detail below with reference to the accompanying drawings, in which Fig. 1 is a diagrammatic cross sectional view of a symmetrical electrochemical cell comprising an electrolyte and two identical electrodes, each electrode including three electrode layers,

[0023] Fig. 2 illustrates the electric connections to the symmetrical cell used for characterizing the polarisation resistance R_P of the electrodes,

[0024] Fig. 3 shows test data in form of an impedance spectrum corrected for the area of the electrode. The polarisation resistance R_P of the electrode presents approximately 2/3 of the distance between the axis points of intersections on the abscissa,

[0025] Fig. 4 shows an equivalent circuit used for curve adjustment of the test data in Fig. 3, where L is an inductance, R_S a serial resistance in the electrolyte, R_1 and R_2 together present the polarization resistance R_P, whereas R_D is the diffusion resistance in the gas above the electrodes. Q is a constant phase element representing a non-ideal capacitance associated with the indicated resistances,

[0026] Fig. 5 is a sectional view through a semi cell for characterising the inplane conductivity of the electrode, where an upper electrode layer of a predetermined thickness has been superposed an electrolyte with an active electrode layer. The thickness of the active electrode layer is preferably less than 20μm,

[0027] Fig. 6 illustrates a contacting so as to characterize the inplane conductivity of an upper electrode layer on the semi cell of Fig. 5. Platinum wires with insulating aluminium pipes wound thereon are pressed against the electrode surface of a weight load. The platinum wires represent four contacts of a square

arrangement, the conductivity of thin layers being measurable between said contacts,

[0028]   Fig. 7 illustrates an arrangement for measuring the catalytic activity of a powdered electrode layer. A gas mixture is established with mass flow valves and is carried successively through the following elements through pipes: A bobble bottle with water on a thermostatically controlled oil bath, whereby the water content in the gas is increased, a powdered catalyst on a bed of inert material in a heated U-shaped quartz pipe, in which a catalytic reaction occurs, a cold trap, in which the water content in the gas is reduced, and a gas chromatograph, in which the composition of the gas is analysed,

[0029]   Fig. 8 shows measuring data, viz. the catalytic activity expressed as the reforming speed versus the content of MnO_X expressed as metal atom% of Mn in the electrode layer,

[0030]   Fig. 9 is a cross sectional view of an electrochemical cell, where an electrolyte has been coated with two cathode layers on one side and two anode layers on the opposite side,

[0031] .   Fig. 10 is a sectional view of an experimental contacting of the cell of Fig. 9. The electrode surfaces of the cell are coated with a non sintered contact layer on both anode and cathode, said layers ensuring the contact to a woven platinum grid which is applied onto both electrode surfaces,

[0032]   Fig. 11 is a sectional view of an arrangement in an oven for an electric characterizing of an electrochemical cell. The contacted electrochemical cell of Fig. 10 has been mounted between gas distribution plates with ribs and openings, said gas distribution plates in turn being mounted between two sets of concentric aluminium pipes. Gases are fed to the electrodes through the outer pipes and removed through the inner pipes,

[0033]   Fig. 12 shows measuring data, viz. area corrected voltage curves for the edge voltage V_K and the central voltage V_c, respectively. The DC resistance of the cell is calculated as the negative average inclination over the entire measured interval.

BEST MODE FOR CARRYING OUT THE INVENTION

[0034]   The addition of MnO_X to the active electrode layer, which preferably represents less than 20μm, and the superposed layers 19, 20, which can be of a predetermined thickness, has been documented by way of a number of examples.

[0035]   The polarization resistance R_P measured at 850°C and 1000°C in hydrogen with 3 % water for an Ni/YSZ cermet anode has been reduced by addition of MnO_X by way of 1) impregnation of a sintered electrode, 2) application onto the electrolyte surface prior to the application and sintering of the electrode, and 3) admixing into the anode slurry prior to application and sintering. At 850°C R_P has been reduced from 105 $m\Omega cm^2$ to 59 $m\Omega cm^2$, and at 1000°C R_P has been reduced from 79 Ωcm^2 to 20 Ωcm^2.

[0036]   The electronic conductivity of an Ni/YSZ electrode layer has been increased by addition of MnO_X from 14 to 390 S/cm at 20°C and from 2.5 to 60 S/cm at 1000°C.

[0037]   The catalytic activity of an Ni/YSZ cermet electrode layer for steam reformation of methane has been reduced by addition of MnO_X from 0.3 to 0.005 $\mu mol min^{-1} g^{-1}$.

[0038] · The polarization resistance R_P of an Ni/YSZ anode on an electrochemical cell has been reduced by addition of MnO_X to the anode from 0.25 Ωcm^2 to maximum 0.08 Ωcm^2 at 850°C.

Below the examples are discussed in detail:

Reduction of R_P for Ni based electrode

[0039]   The electrodes are applied onto the electrolyte by way of airborne injection of a particle suspension, but other techniques, such as serigraphy and painting are also suitable. The suspension is provided in the solvent ethanole by means of the dispersant polyvinyl butyral, but other solvents and dispersants are also suitable. An electrode comprises one or more layers, and particle suspensions of different compositions can be used for these layers. A suitable particle size distribution and homogeneity are obtained by ball grinding the suspension. After spraying of one or more particle suspensions, the electrode is subjected to a

sintering. The electrode can furthermore be admixed additives by way of application of intermediate layers or postimpregnation by means of dissolved salts or suspensions.

[0040]   In order to illustrate the effect of adding MnO_x to Ni based electrodes, a reference electrode without MnO_x and test electrodes with MnO_x have been produced, cf. Table IA. The electrodes comprising a first, a second and a third electrode layer 18, 19, 20 are applied onto both sides of sintered 8YSZ (ZrO_2 doped with 8 mol % Y_2O_3) electrolytes 1, cf. Fig. 1. The electrolytes 1 are of a thickness of 160 to 180 μm. A contact face 22 (shown in Fig. 2) is provided between the electrolyte 1 and the first electrode layer 18. The produced cells are fragmented into almost square elements of an area of approximately 0.1 to 0.2 cm_2 and mounted between four platinum wires 6 in such a manner that two elements are provided on the central portion of each electrode surface, cf. Fig. 2. The cells are placed in an oven in a controlled atmosphere of hydrogen moistened with 3% water at 25°C. The impedance of the cells is measured by impedance spectroscopy at open voltage ($\eta=0$) at 850°C and 1000°C. Such a measuring is illustrated in Fig. 3.

[0041]   A curve adjustment of the impedance measurements were performed by means of the program "Equivalent Circuit", an equivalent circuit being adjusted to the test data. The equivalent circuit includes capacitances C, inductances L, resistances R and constant phase elements Q.

[0042]   The equivalent circuit used for the curve adjustment is shown in Fig. 4, where L is an induction also covering phase errors in the measuring equipment at high frequencies, R_S is a serial resistance including a resistance substantially in the electrolyte, R_1 & Q_1 and R_2 & Q_2 represent limiting steps in the electrode reaction, whereas R_D & Q_D represents the gas phase diffusion resistance outside the anode structure. The reaction resistance R_P is then calculated for the electrode as

[0043] $R_P = (R_1 + R_2) A \ 1/2$

[0044]   where A is the area of the cell, and the factor $1/z$ is caused by both electrodes on the cell being part of the measuring.

Table IA

Type of element	The composition of the first layer, metal atom%	Sintering and thickness	The composition of the following layer, metal atom%	Sintering and thickness	R_P, 850°C, $m\Omega cm^2$	R_P, 1000°C, $m\Omega cm^2$
Reference element	67.5% NiO, 32.5% 8YSZ	1300°C/2h 15 μm	67.5% NiO, 32.5% 8YSZ	2 x 1300°C/2h 35 μm	105	79
Impregnation after sintering	65.8% NiO, 31.8% 8YSZ, 2.4% MnO₂	1300°C/2h 15 μm	65.8% NiO, 31.8% 8YSZ, 2.4% MnO₂	2 x 1300°C/2h 35 μm	86	20
Additive on the electrolyte surface	64.4% NiO, 31.0% 8YSZ, 4.6% MnO₂&	1300°C/2h 10 μm	67.5% NiO, 32.5% 8YSZ	2 x 1300°C/2h 37 μm	74	43
Additive in anode layer	67.5% NiO, 32.5% 8YSZ, 2.1% MnO₂#	1300°C/2h 5 to 6 μm	67.5% NiO, 32.5% 8YSZ	2 x 1300°C/2h 50 μm	59	66

□ Mn added as solution of $Mn(Ac)_2$ $4H_2O$ by impregnation of the sintered electrode structure.

& Mn added as solution of $Mn(Ac)_2$ $4H_2O$ painted on electrolyte prior to spraying of first anode layer.

Mn added as solution of $Mn(NO3)_2$ $4H_2O$ in the particle solution forming the first electrode layer.

Improved conductivity of Ni/doped ZrO, based electrode

[0045]   The conductivity in the plane of the electrode can be a limiting factor for the conductivity of said electrode when the distance between contact points to the surrounding contacting structure exceeds the thickness of the electrode structure. The latter is often the case where gas access to the electrode is required. It is typically necessary to apply a nickel based layer onto an electrochemical cell with a nickel based active electrode of a poor thickness, i.e. below 20 μm, in order to ensure a sufficient inplane conductivity.

[0046]   Such a composite electrode layer can be applied by way of spraying of a particle suspension as stated above. Other techniques are also suitable. After the application of one or more particle suspensions, the structure can be subjected to a sintering, if necessary.

[0047]   In order to document the positive effect of MnO_X on the inplane conductivity of a composite nickel based electrode layer, two Ni/8YSZ (ZrO_2 doped with 8 mol% Y_2O_3) electrode layers are produced with and without MnO_x. The comparison appears from Table 1B. The electrode layers are sprayed onto 10 to 20 μm thin Ni/8YSZ anodes on 8YSZ electrolytes, cf. Fig. 5 showing the electrolyte 1, onto which an active electrode layer 23 and an electrode layer 24 have been applied.

[0048]   The produced semi-cells are fragmented into elements of an area of approximately 1 to 2 cm^2, and four Pt point connections are established by means of weight loaded Pt wires 6 wound about aluminium pipes 7, cf. Fig. 6 showing the weight load 26. The element is placed in an oven in an atmosphere of 9 % hydrogen in nitrogen with 3% water, and heated to 1000°C. The conductivity of the electrode layer 8 a(at 1000°C) is determined by way of a square four point measuring (Van der Pauw) technique, which is calibrated on a metal element having a well known conductivity.

[0049]   After the above characterization the elements are cooled under reducing conditions, and the conductivity thereof at room temperature a(20°C) is determined by way of a conventional linear four point conductivity measuring.

Table IA

Type of element	The composition of the first layer, metal atom%	8YSZ Particle size	Sintering	σ(20°C), S/cm	σ(20°C), S/cm
Reference element	67.5% NiO, 32.5% 8YSZ	20% 0.3 to 0.4 μm 80% 10 to 50 μm	1250°C/2h	470	50
Test element	64.5% NiO, 31.9% 8YSZ, 4.1% MnO₂#	20% 0.3 to 0.4 μm 80% 10 to 50 μm	1250°C/2h	1060	150
Reference element	67.5% NiO, 32.5% 8YSZ	40% 0.3 to 0.4 μm 60% 10 to 50 μm	1250°C/2h	13	2.5
Test element	64.5% NiO, 31.9% 8YSZ, 4.1% MnO₂#	40% 0.3 to 0.4 μm 60% 10 to 50 μm	1250°C/2h	390	60

\#   Mn added as solution of $Mn(NO3)_2 \cdot 4H_2O$

Catalytic activity of Ni based electrode

[0050]   For nickel based electrodes and catalytic elements, where an electronic
conductivity is to be maintained while the catalytic activity of nickel is to be
limited, it is not possible to reduce the amount of nickel much below 30% in a
porous structure.

[0051]   Instead the catalytic activity of present nickel can be reduced. Below it
has been documented that this reduction of catalytic activity for nickel can be
provided by adding MnO_x. A fine grained Ni/8YSZ (ZrO_2 doped with 8 mol%
Y_2O_3) based structure is produced by mixing NiO, 8YSZ and a water based binder
with water to a viscous mass and by rolling this mass into a plate of a thickness of
1 mm and sintering said plate at 1350°C/8 hours. A number of such plates has
been produced by admixing various amounts of $Mn(NO_3)_2$ $4H_2O$. The tested
compositions appear from Table 1C. The sintered plates are crushed in a mortar,
and by way of screening a fraction of 0.4 to 1.0 mm has been removed and tested
as catalyst for steam reforming of methane.

[0052]   The catalyst is admixed quartz sand in the ratio 1:5. This mixture is
placed on a bed of pure quartz sand in a U shaped quartz pipe ($Ø_i$=5mm), through
which a gas mixture is fed to a gas chromatograph, cf. Fig. 7. The gas mixture is
established by a mixing of pure gases through thermal mass flow meters.
Subsequently the gas is moistened with water in a bobble bottle 9 on a
thermostatically controlled oil bath 10. Thereafter the gas is kept at an increased
temperature until it has passed the catalyst 11 followed by a quartz ring 27 so as to
prevent condensation. The quartz pipe 12 is placed in an oven 13, and the sample
is heated to 900°C in a flow of 9% hydrogen in nitrogen. The sample is stabilised
for 24 hours in pure hydrogen with approximately 3% water (saturation at 25°C)
and then cooled to 850°C. The gas in the pipe is replaced by 67% methane + 33%
water (saturation at 88°C). When the gas has passed the catalyst 11, the majority
of the water is condensed out into a cold trap 15 (8°C), and the composition of the
remaining amount of gas is tested in a gas chromatograph 16. The gas
chromatograph 16 (HP 5890 Series II) is equipped with a 6 foot Porapak Q
column, a detector measuring thermal capacity (TCD), as well as an HP3396A

integrator. The reformed portion of the methane gas R_{CH4} is calculated on the basis of a carbon balance in the gas leaving the catalyst 11,

[0053] R_{CH4} $(C_{CO2} + C_{CO})/(C_{CO2} + C_{CO} + C_{CH4})$

[0054]   where C_X indicates the concentration of methane (C_{CH4}), carbon dioxide (C_{CO2}) and carbon monooxide (C_{cO}), respectively. R_{CH4} is standardized relative to the weighed amount of Ni/8YSZ catalyst and the composition and speed of the input gas in the pipe surrounding the catalyst 11, whereafter the reforming speed in $\mu molmiri^{-1}g^{-1}$ are found. The calculated values based on the measurements are indicated in Fig. 8.

Table 1 C

Type of element	Composition of the catalyst, metal atom%	Sintering
Reference element	67.4% NiO, 32.6% 8YSZ	1350°C/8h
Test element	65.0% NiO, 31.4% 8YSZ, 3.6% MnO_2#	1350°C/8h
Test element	65.0% NiO, 31.4% 8YSZ, 3.6% MnO_2#	1350°C/8h

Added as $Mn(NO_3)_2$ $4H_2O$

Demonstration of electrochemical cell

[0055]   For the power production of a fuel gas and air, an electrochemical cell, cf. Fig. 9, with MnO_X is produced in the following manner:

[0056]   A compact 8YSZ (ZrO_2 doped with 8 mol % Y_2O_3) electrolyte of a thickness of 170μm is produced by sintering at 1350°C after film casting.

[0057]   A particle suspension containing 55.8 w/o of 8YSZ and 44.2 w/o of NiO is sprayed onto one electrolyte side, viz. the anode side, and sintered at 1300°C/2h, which results in a porous layer of a thickness of approximately 15μm.

[0058]   A second particle suspension containing 42.6 w/o of 8YSZ and 53.6 w/o of NiO and 3.8 w/o of MnO_2 (3.9 metal atom%) added in form of $Mn(NO_3)_2$ $4H_2O$ is sprayed twice onto the initially applied layer on the anode side and sintered after each spraying at 1200°C/2h, whereafter it forms a porous layer of a thickness of approximately 35 μm.

[0059] A third particle suspension containing 40 w/o of 3YSZ and 60 w/o of $(La_{0,85}Sr_{0,15})_{0,90}MnO_3$ is sprayed onto the opposite side of the electrolyte, viz. the cathode side, and sintered at 1100°C/2h, whereafter it forms a porous layer of a thickness of approximately 10 µm.

[0060] A fourth particle suspension containing $((La_{0,85}Sr_{0,15})_{0,90}MnO_3)$ is sprayed onto the active cathode in two layers, each layer being sintered at 1100°C/2h, whereafter it forms a porous layer of a thickness of approximately 30 µm.

[0061] The efficiency of the cell is characterized as follows, cf. Fig. 10.

[0062] The anode side is provided with a contact layer in form of an NiO suspension which is sprayed thereon in a layer of a thickness of approximately 50 µm and which is not sintered.

[0063]

[0064] The cathode side is provided with a contact layer in form of a 75 µm thick film cast layer, which is applied by way of softening in ethanole, and which is not sintered.

[0065] Circular, woven Pt grids 29 of an area of 10.0 cm^2 are symmetrically mounted on both electrode surfaces.

[0066] As a result the cell is efficiently contacted across the entire electrode surface through the platinum grids 29.

[0067] The cell with the contacting is mounted between two plane gas distribution plates 30 with openings and ribs which ensure gas access to the electrodes. The cell and the contacting and the gas distribution plates 30 are mounted between two sets of aluminium pipes 31 in an oven, cf. Fig. 11. The cell is heated to a temperature of 1050°C. The temperature is measured by means of thermal elements arranged 1 mm above the centre of the cell.

[0068] The cathode side is fed with air, whereas the anode side is fed with hydrogen moistened with 1.2% water at 11°C. The gases are fed through the outer pipes and removed through the inner pipes. The voltage across the cell can be measured at the edge V_K and the centre V_c of the electrodes through wires without current. Current is collected from the cell through the platinum grids 29 and

separate conduits by loading with external resistances, and a current voltage curve, cf. Fig. 12, can be taken. The negative inclination of the current voltage curve presents the DC resistance of the cell, here approximately 0.63 Ωcm^2 estimated conservatively across the entire measured interval.

[0069]   The DC resistance of the cell includes a) electrolyte resistance (estimated to be 0.35 Ωcm^2 for 170 μm 8YSZ at 850°C, b) the reaction resistance of the cathode (estimated to 0.20 Ωcm^2 as the optimal measuring for this type of cathode), c) the reaction resistance of the anode, and d) the resistance in the contacting of the cell. The measuring d) cannot be measured separated, and it is here assumed to be 0.00Ωcm^2. Subsequently, maximum 0.08Ωcm^2cmz of the DC resistance of the cell remains, which can be ascribed to the Ni based anode, which has been admixed MnO_x.

[0070]   Reference cells are produced in the same manner apart from 1), MnO_x has not been added, and 2) the two outermost anode layers have been sintered at 1300°C/2h in order to ensure the conductivity in stead of only 1200°C/2h, and 3) the cathode has been sintered at 1300°C. These reference cells provide in connection with an identical test at best a DC resistance of 1.00 Ωcm^2. It is possible to derive a reaction resistance of the anode of 0.25 Ωcm^2 from the latter in the same manner when it comes to Ni- based anodes without the addition of MnO_x.